



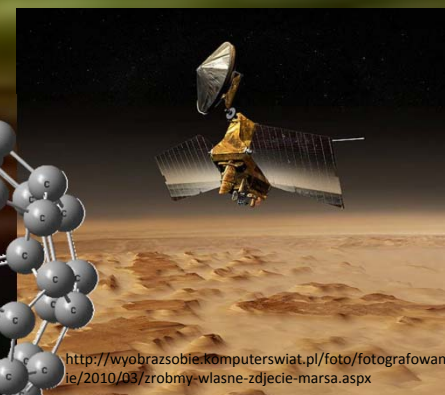
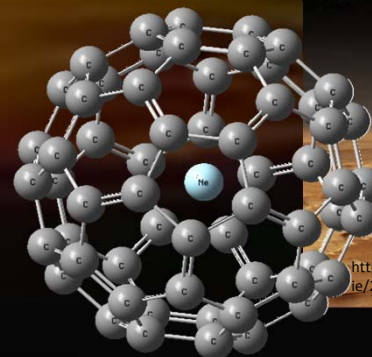
# Sensitivity of noble gases to carbon nanosystems

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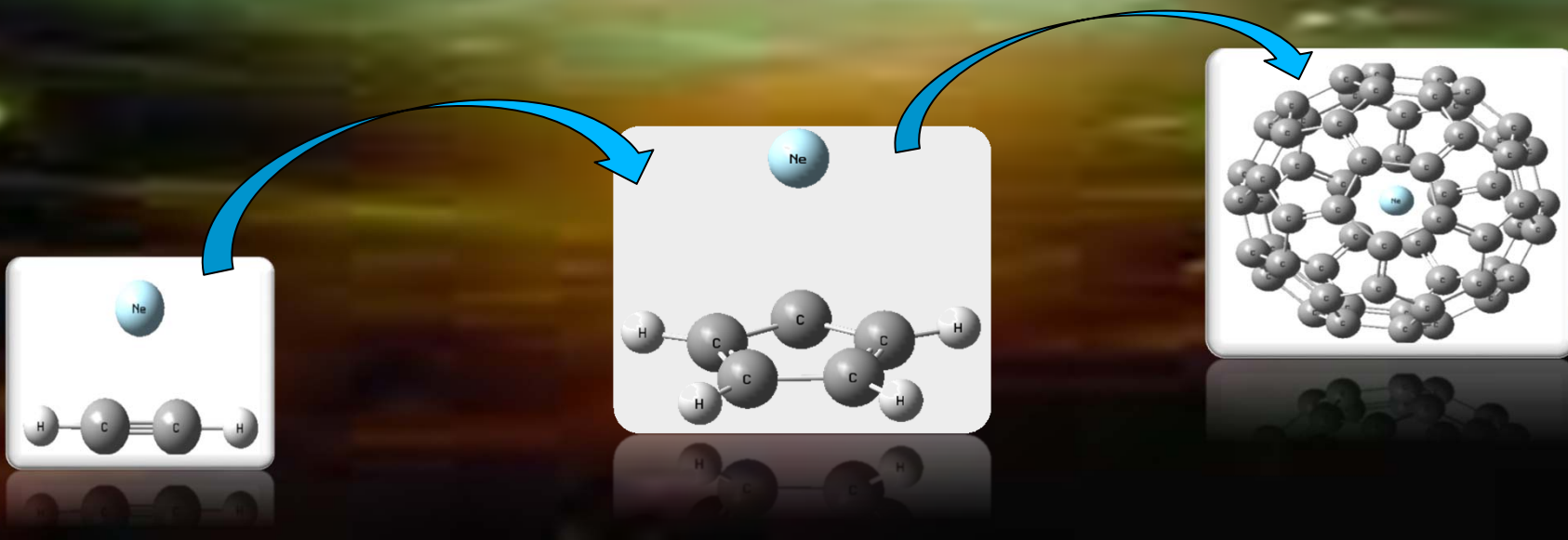
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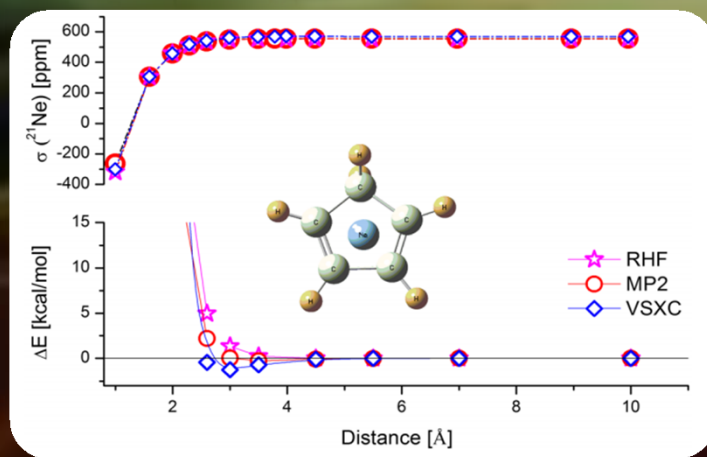
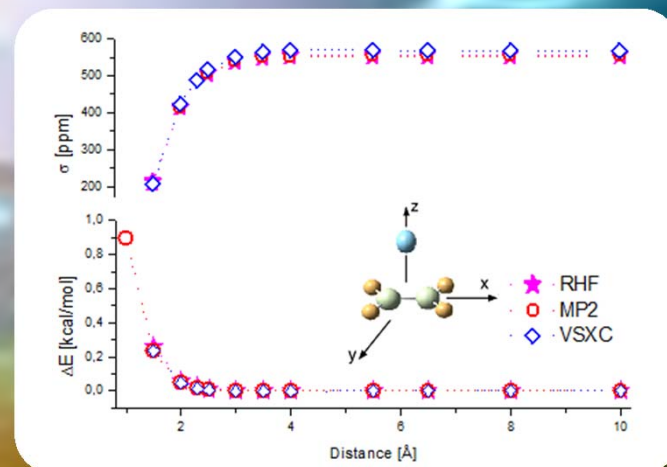
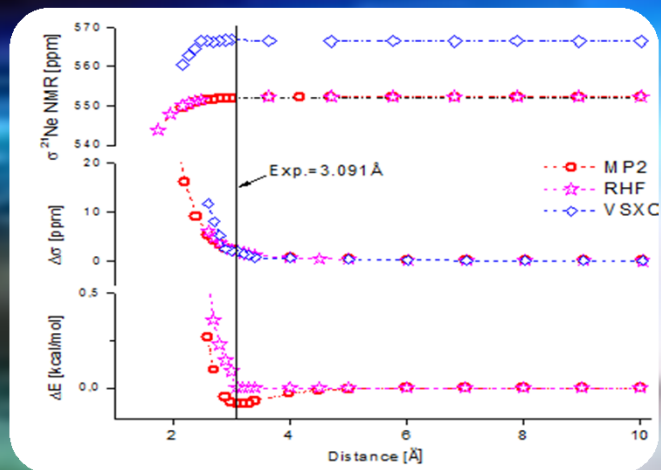
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# Noble gases as a probes

Due to their unique NMR properties, the noble gases (Ng) are a very interesting hydrophobic probes of environment polarity and structure. Ng atoms could be used as spherical NMR probes, free from specific interactions, including H-bonding or association in solution. Despite the fact that noble gases are good candidate to use as NMR probes, the spectroscopic studies using magnetically active Ng isotopes are not so common.



# Sensitivity of $^{21}\text{Ne}$ NMR parameters



# Sensitivity of noble gases to carbon nanosystems

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Due to their unique NMR properties, the noble gases (Ng) are a very interesting hydrophobic probes of environment polarity and structure. Ng atoms could be used as spherical NMR probes, free from specific interactions, including H-bonding or association in solution. Despite the fact that noble gases are good candidate to use as NMR probes, the spectroscopic studies using magnetically active Ng isotopes are not so common.

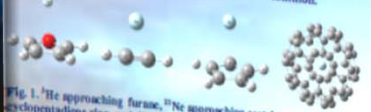


Fig. 1. <sup>3</sup>He approaching furane, <sup>20</sup>Ne approaching acetylene and 1,3-cyclopentadiene ring and <sup>20</sup>Ne inside fullerene C<sub>60</sub>.

The main goal of the present study is to accurately predict isotropic nuclear magnetic shielding and related chemical shift and shielding anisotropy of <sup>3</sup>He, <sup>21</sup>Ne in its gas form (as an individual atom), dimer (like in liquid helium at extremely low temperatures) and in contact with several model carbon systems. The sensitivity of <sup>21</sup>Ne NMR parameters of a single neon atom moving toward multiple CC bond in C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and inside C<sub>20</sub>, C<sub>28</sub>, C<sub>32</sub>, C<sub>34</sub> and C<sub>60</sub> fullerenes was studied. In addition <sup>3</sup>He with furane model was studied.

Table 1. VSXC/pC-S-2 calculated <sup>21</sup>Ne NMR chemical shift of a single neon atom confined inside fullerene cage of different size and symmetry.

Molecule	Shift tensor components				Isotropic shielding	Shielding anisotropy	Chemical shift (ppm)
	$\sigma_{xx}$	$\sigma_{yy}$	$\sigma_{zz}$	$\sigma_{xy}$			
Ne gas	569 080	569 080	569 080	569 080	1 000	0 000	0 000
Ne <sub>2</sub>	568 620	568 620	570 620	569 108	1 626	-2 008	-2 008
Ne at C <sub>28</sub>	44 523	370 872	636 871	350 755	429 174	218 524	218 524
Ne at C <sub>28</sub> D <sub>2d</sub>	474 213	481 311	495 421	485 315	15 159	81 763	81 763
Ne at C <sub>32</sub> D <sub>2d</sub>	474 123	489 287	475 047	477 144	66 555	31 736	31 736
Ne at C <sub>32</sub> D <sub>2h</sub>	386 535	498 771	481 568	426 260	48 312	141 730	141 730
Ne at C <sub>34</sub> C <sub>2v</sub>	383 303	467 253	497 898	449 498	72 600	119 589	119 589
Ne at C <sub>60</sub>	489 828	497 529	501 687	496 261	8 110	32 799	32 799

**Conclusions**  
 Theoretically predicted <sup>3</sup>He, <sup>21</sup>Ne NMR parameters calculated at RHF, MP2 and DFT levels of theory are sensitive to surrounding effect. In particular to the presence of  $\pi$ -electrons and lone electron pairs in furane, selected as an example of a small heterocyclic structure. The calculated changes of isotropic nuclear magnetic shieldings and its shielding anisotropies are good indicators of interaction of Ng probe (here helium-3) with heterocyclic molecules containing oxygen atom. The RHF and MP2 predicted neon isotropic shieldings and shielding anisotropies are very close to earlier benchmark CCSD and CCSD(T) results for helium gas and liquid, modeled by single atom and its dimer.

**Acknowledgments**  
 Marzena Nieradka is a recipient of a Ph.D. fellowship from a project funded by the European Social Fund Stypendia doktoranckie-inwestycja w kadre naukową województwa opolskiego. T. Kupka was supported by the Faculty of Chemistry, University of Opole [grant number 8/WCH/2013-S].

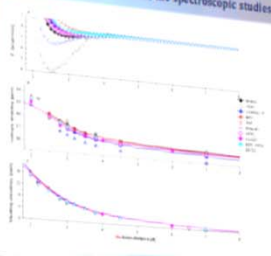


Fig. 2. (A) Interaction energy, (B) nuclear shielding and (C) shielding anisotropy of <sup>3</sup>He atom approaching furan ring predicted using DFT, DFT-G, RHF and MP2 methods. Energy scan was performed with smaller basis set (6-311+G\*) and fairly large and flexible pC-S basis set was used for NMR calculations.

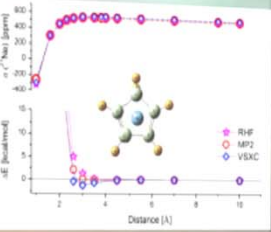


Fig. 3. The RHF, MP2 and VSXC-calculated isotropic nuclear magnetic shieldings and interaction energies (E in kcal/mol) of Ne atom interacting with 1,3-cyclopentadiene (pC-S basis set is used).

**References:**  
 [1] M. Straka, F. Lantini, J. Viera, *J. Phys. Chem. A* 112, 2458 (2008).  
 [2] M. Straka, J. Viera, *J. Phys. Chem. A* 110, 12338 (2006).  
 [3] P. Stępanek, F. Bant, M. Straka, *Chem. Phys. Lett.* 500, 54 (2010).  
 [4] T. Kupka, M. Nieradka, J. Kaminskiy, L. Stobinski, *Magn. Reson. Chem.* 51, 674 (2013).  
 [5] T. Kupka, M. Strachó, L. Stobinski, J. Kaminskiy, *Magn. Reson. Chem.* 51, 643 (2013).  
 [6] T. Kupka, M. Strachó, M. Nieradka, J. Kaminskiy, *J. Chem. Theor. Comput.* 6 (2010) 1580-1589.  
 [7] D. Cappellati, M. Bartolomei, F. Pirani, V. Aquilanti, *J. Phys. Chem. A* 104, (2002).

# Zapraszamy do posteru!



**Acknowledgments**  
 Marzena Nieradka is a recipient of a Ph.D. fellowship from a project funded by the European Social Fund Stypendia doktoranckie-inwestycja w kadre naukową województwa opolskiego. T. Kupka was supported by the Faculty of Chemistry, University of Opole [grant number 8/WCH/2013-S].

